The Anomalous Osmose of Solutions of Electrolytes with Collodion Membranes

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A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE UNIVERSITY OF MICHIGAN

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Dwight Clark Carpenter

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THE ANOMALOUS OSMOSE OF SOLUTIONS OF ELECTROLYTES WITH COLLODION MEMBRANES

BY DWIGHT CLARK CARPENTER

I. HISTORY

The phenomenon of osmosis, or the unequal rate of passage of two liquids through a membrane which separates them, was discovered by the Abbé Nollet[1] in 1748. After filling a vessel with alcohol, closing the orifice with bladder, and submerging in pure water, he observed that the bladder became distended, thereby showing that water had passed through the membrane more rapidly than alcohol.

This observation attracted little attention of scientists for over half a century, and was evidently forgotten until Sommering,[2] experimenting with a pig's bladder, made a similar discovery. He found that when a pig's bladder, filled with an alcohol-water solution was suspended in air, the alcohol became more concentrated. When the experiment was repeated substituting a rubber bag for the bladder, the alcohol became more dilute. This appears to have been the first recorded observation of anomalous osmose. The above effects, the opposite of each other, established the important fact that the nature of the membrane material itself was an influencing factor.

The first quantitative experiments on osmosis were carried out by Dutrochet[3] and Vierordt[4] between the years 1826 and 1848. They both found that when a salt solution was separated from water by a membrane of pig's bladder, the water passed through the membrane more rapidly than the salt solution, resulting in a hydrostatic pressure. As this pressure

[1] Nollet: Memoires de l'Academy Roy des Sciences, **1748,** 57–104.
[2] Sommering: Pogg. Ann., **28,** 17 (1814).
[3] Dutrochet: Ann. Chem. Phys., **35, 37, 48, 49, 51, 60.**
[4] Vierordt: Pogg. Ann., **73,** 519 (1848).

was the result of osmosis, it was termed osmotic pressure. It was early recognized that the experimentally determined pressure was a resultant of the movement of both the solution and the water. Dutrochet gave us our nomenclature of these two oppositely moving liquids. The flow inward toward the more concentrated side, he called the endosmotic current, and the outward flow, the exosmotic current. The terms osmose and osmosis are now used to denote the process as a whole. In 1827 Dutrochet[5] announced an electrical theory to explain osmosis. He believed that the two sides of the membrane developed different "degrees of electricity," but that this difference could not be detected with a galvanometer.

The work of Dutrochet and Vierordt showed that the rate of passage of pure water through the membrane depended not only on the salt used, but also on the concentration of the salt solution. From his later experiments with porous inorganic membranes, Dutrochet concluded that osmosis was also dependent on the nature of the membrane used.

A number of explanations to account for this phenomenon were brought forward by various investigators. Poisson[6] believed that capillarity was the determining factor in osmosis. Brücke[7] considered it due to relative "attraction" of the membrane for the two liquids. Jolly[8] advanced a theory of hydrodiffusion, in which he claimed that the exosmotic current was replaced by the endosmotic current of water, which was characteristic of water and independent of the concentration. His final conclusion was that, in a given time, the amount of diffused substance was dependent on membrane area, the density of the solution, and the attraction of the separated substances for the membrane and for each other. Almost simultaneously, Liebig[9] gave reasons for believing that osmose was due to the ability of the membrane to absorb the separated liquids. This directed the trend of investigation toward

[5] Dutrochet: Ann. Chem. Phys., **35,** 393 (1827).
[6] Poisson: Ibid., **35,** 98 (1827).
[7] Brücke: Pogg. Ann., **58,** 27 (1843).
[8] Jolly: Ibid., **78,** 261 (1849).
[9] Liebig: Ann. Chem. Phys., (3) **25,** 367 (1849).

the study of different membranes and their function in the osmotic process.

Thomas Graham[10] in 1855 published much data on osmosis with both organic and inorganic membranes. He advanced the theory that an alteration of the membrane was an indispensible condition to the maintenance of the "osmotic force." He thought one side of the membrane was always acid and the opposite side alkaline, and that the direction of the endosmotic current was from the acidic to the basic side; or when the osmose of acids and bases were tested, the direction of flow was alway toward the side of lesser acidity in the former case, and toward the more basic side in the latter. In the development of this generalization, Graham did not include the results he obtained with porous earthenware membranes, for the reason that the osmotic effects observed with these membranes were usually opposite to the effects obtained with organic membranes. He had no satisfactory explanation to account for this difference. Later, influenced by his own work on dialysis and by that of L'Hermite[11] on selective or preferential solubility of two liquids in a separating membrane, Graham came to the same conclusions as those of Liebig.

M. Trabue[12] prepared a membrane from a non-setting glue treated with tannic acid, which was the first artificial septum, permeable to water but impermeable to a crystalloid. He also prepared a number of precipitation membranes of different permeability. Pfeffer[13] devised the method of forming precipitation membranes within the walls of porous earthenware, thereby forming cells which were capable of withstanding great pressures. With these cells Pfeffer performed his classic experiments on the osmotic pressure of sugar solutions. His work proved that the osmotic pressure varied as the sugar concentration varied. Many investigators have since confirmed Pfeffer's measurements.

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[10] Graham: Ann. Chem. Phys., (3) **45,** 17 (1855).

[11] L'Hermite: Ibid., (3) **43,** 420 (1855).

[12] Traube: Archiv. Anat. Phys. Und Wissensch. Medizin., **1867,** 87.

[13] Pfeffer: Osmotische Undersuchungen, Leipzig, 1877.

Up to this time Van't Hoff[14] had been studying gases and chemical equilibrium in solution with a view of throwing light on the question of chemical affinity. He recognized the close analogy between gases and dilute solution. This analogy between the behavior of such widely differing materials, led him to turn his attention to Pfeffer's data on the osmotic pressure of dilute solutions and to compare osmotic pressure with gas pressure. From Pfeffer's data he showed that the osmotic pressure of a dilute solution was equal to the pressure which the dissolved substance would exert if present in the gaseous state and present in the same volume as that occupied by the solution. This generalization has been extended to electrolytes by taking into account the increased number of solute particles produced by the dissociation of the electrolyte in solution. Van't Hoff was not concerned with the mechanism of osmosis, but simply in the quantitative relationships existing between gaseous and osmotic pressures.

The majority of investigators in the field of osmosis, since the time of Van't Hoff, have directed their attention to the cause of osmosis and membrane permeability. L'Hermite[11] offered the first explanation of membrane permeability. His theory was that of selective or preferential solution of the two separated liquids in the membrane. Traube[12] believed that semipermeable membranes acted like atomic sieves, permitting molecules of a certain size to pass through but preventing the passage of larger particles. However it has been demonstrated by Bigelow and Bartell,[15] later by Bartell,[16] and again by Bigelow and Robinson,[17] and also by Tinker,[18] that osmotic phenomena were obtainable with membranes the pore diameters of which were much larger than molecular dimensions. H. E. Armstrong[19] advanced the theory that some kind of chemical association between the membrane pores

[14] Van't Hoff: Zeit. Phys. Chem., **1,** 481 (1887).
[15] Bigelow and Bartell: J. Am. Chem. Soc., **31,** 1194 (1909).
[16] Bartell: J. Phys. Chem., **15,** 659 (1911).
[17] Bigelow and Robinson, Ibid., **22,** 99, 153 (1918).
[18] Tinker: Proc. Roy. Soc., **92A,** 357 (1916).
[19] Armstrong: Ibid., **81B,** 94 (1909).

and water took place which prevented the passage of any hydrolated molecules of solute but had no effect on unhydrolated substances. The most generally accepted explanation has been that of L'Hermite, whose view has been supported by a large number of experiments described by Nernst,[20] Kahlenberg,[21] Flusin,[22] and others.

According to Findley,[23] theories accounting for osmosis have generally fallen into two classes. One, the kinetic interpretation, considers that osmotic pressure is due to bombardment of the semipermeable membrane by the imprisoned solute molecules, analogous to the kinetic explanation of gaseous pressure. The other view is that the osmotic pressure is the hydrostatic pressure produced by the passage of solvent into the solution. This latter explanation has been the most useful in the experimental study of osmosis, and defines the osmotic pressure as the hydrostatic pressure produced by the entrance of solvent into the solution. In negative osmose, the reverse is the case.

The mechanism of the osmotic process has been explained in many ways. In 1891 Jäger[24] proposed the surface tension theory. Although the theory has since been subjected to numerous modifications, in its simplest form, it stated that the osmotic pressure was proportional to the difference in surface tension between the solution and the pure solvent. Several years after this, Callender[25] proposed the vapor pressure hypothesis, according to which the membrane capillaries were regarded as not wetted by liquids, but rather that they acted as vapor pressure sieves. Perrin[26] and Girard[27] considered that osmosis was controlled chiefly by electrostatic phenomena.

It must be borne in mind that Van't Hoff's generalization

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[20] Nernst: Zeit. Phys. Chem., **6,** 35 (1890).

[21] Kahlenberg: J. Phys. Chem., **10,** 141 (1906).

[22] Flusin: Ann. Chem. Phys., (8) **13,** 480 (1908).

[23] Findley: Osmotic Pressure, p. 99 (1919).

[24] Jäger: Weiner, Ber., **100,** 245, 493 (1891).

[25] Callender: Proc. Roy. Soc., (A) **80,** 466 (1908); Proc. Roy. Inst., **19,** 485 (1911).

[26] Perrin: Compt. rend., **136,** 1388 (1903).

[27] Girard: Ibid., **146,** 927 (1908); **150,** 1444 (1910); **153,** 401 (1911).

was developed from Pfeffer's data on the osmosis of dilute sugar solutions, and was applied rigidly only to such dilute non-electrolytes, and only in the case of perfectly semipermeable membranes. Such membranes are seldom realized in actual practice, and in the vital processes of living organisms, the group of cells which seem to act as osmotic membranes, are more or less permeable to the solute. The tendency of electrolytes to produce osmotic pressures of serious non-conformity to the gas laws has often been detected when refined measurements were made. Lord Berkeley and E. G. J. Hartley[28] found abnormal osmotic pressures with solutions of calcium, strontium and potassium ferrocyanides, and to explain these anomalies they assumed that the salts existed as ionized double molecules. H. N. Morse[29] found that membranes which proved satisfactory for finding the osmotic pressure of sugar solution, failed to give the quantitative results expected with alkali chlorides. Moreover after standing for some time with these chloride solutions in them, the cells were greatly impaired for use again with sugar. A cell returned very nearly to its original condition after soaking in water for several months. Fouard[30] and others have noticed this same lack of agreement between the experimental and calculated osmotic pressures of solution of electrolytes.

This anomalous behavior of solutions of electrolytes has more often been noticed by the biologist and physiologist than by the chemist. The striking behavior of salt solutions with cells and tissues in the presence of acid or alkali, has been a problem, difficult of explanation and has been studied by Loeb,[31] Osterhout,[32] Lillie,[33] Girard,[34] and others. The swelling of

[28] Berkeley and Hartley: Phil. Trans., (A) **209,** 177, 319 (1908).

[29] Morse: Osmotic Pressures of Aqueous Solutions, Carnegie Institution of Washington, p. 211–217 (1914).

[30] Fouard: Bull. Soc. Chem., (4) **11,** 249–261 (1912).

[31] Loeb: Science, **37,** 428 (1913).

[32] Osterhout: Biol. Chem., **19,** 493, 561 (1914).

[33] Lillie: Am. Jour. Physiol., **194,** (1911).

[34] Girard: Compt. rend., **148,** 1047, 1186 (1909); **151,** 99 (1910); **153,** 946 (1911); J. Phys. Path. Gen., **13,** 359 (1911); Compt. rend., **155,** 308 (1912); **156,** 1401 (1913); **159,** 376 (1914); 167, 351 (1918); **168,** 1335 (1919); **169,** 92 (1919).

muscular tissue and of typical gels has been studied by M. Fischer,[35] Lloyd,[36] and others. Girard studied the osmotic pressures of electrolytes with porous $CrCl_3$, gelatin, frog skin and other membranes. He found that the osmotic pressure of electrolytes varied greatly with their nature, as well as with their concentration. He obtained different results with different membranes, and in some cases recorded even negative osmose. Bartell[37] also observed both positive and negative effects at various concentrations of acetates, chlorides, nitrates and sulfates when porcelain membranes were used. In seeking an explanation of this type of anomalous behavior, Girard enunciated his electrostatic theory. He considered the osmosis of electrolytes to be essentially due to electrical influences and the osmotic process to be dependent upon the same general causes as electro-osmose, namely to the sign of the electrically charged, movable, liquid layer adjacent to the oppositely charged walls of the membrane capillaries, and to the potential difference existing between the two faces of the membrane. He considered the charge on the capillary wall to be due to a small excess of hydrogen or hydroxyl ions, the movable liquid layer assuming an equal but opposite charge. Later work convinced him that the membrane charge could be altered by ions other than hydrogen and hydroxyl. Girard found that the contact potential between two solutions may be raised or lowered, or that the orientation of the potential might even be reversed by the intercalation of a membrane. Other examples of such potential differences exhibited by membranes are found in the work of Loeb,[38] Brunnings,[39] Lillie[40] and Beutner[41]. Thus the membrane seems to play an important part in determining the nature of the osmotic effect and of the electrical state of the cell system. This indicates a close relationship be-

[35] Fischer: Oedema and Nephritis, **1915**.
[36] Lloyd: Proc. Roy. Soc., **89B,** 277 (1916); Biochem. J., **14,** 147 (1920).
[37] Bartell: J. Am. Chem. Soc., **36,** 646 (1914).
[38] Loeb: Science, **34,** 884 (1911).
[39] Brunnings: Pfluger's Archiv., **48,** 241 (1903); **117,** 409 (1907).
[40] Lillie: Loc. cit.
[41] Beutner: J. Phys. Chem., **17,** 344 (1913).

tween electro-osmose and ordinary osmose. The most striking similarity between the two phenomena is found in the reversal of flow of liquid and in the resulting change of the cell potential due to the effect of acid, base and polyvalent ions. The relationship existing between the hydrostatic pressure and the E. M. F. of the electro-osmotic cell system has been stated by Wiedemann,[42] briefly as follows,—for a given material, the difference in hydrostatic pressure maintained between the two sides of a porous diaphragm is proportional to the applied potential.

Wiedemann[43] stated that Munch obtained reversal of flow to the anode with dilute solutions of both neutral and acidified K_2CrO_4. Perrin[26] from his work on electro-osmose came to the conclusion that the acidity or alkalinity of the solution was one of the important factors. With a membrane of porous chromic chloride, acid solutions flowed to the anode while alkalies flowed to the cathode. He also found with cotton wool as a diaphragm that both acids and alkalies flowed to the cathode, and that as the concentration of an acid was increased, the flow decreased, but did not reverse in direction. Larguier des Bancels[44] found that diaphragms of wool, silk and cotton cloth were electro-negative against water. The negative charge of each was increased by alkali and no reversals were observed in acid solutions except with silk in .01 M. HCl. Barrett and Harris[45] found no reversal with agar or parchment membranes, but record the acid—alkali reversal with gelatin which was similar to silk. Engelmann[46] found similar variations in electro-osmose with porous clay, frog's skin, pig's bladder, cat's lung and potato. It is manifestly evident that membranes which are protein substances, more or less amphoteric in general character, appear to show the acid-alkali reversal with greater regularity than other membrane substances. Perrin's laws of contact elec-

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[42] Wiedemann: Pogg. Ann., **87,** 321 (1852); **99,** 177 (1856).
[43] Wiedemann: Elektricitat., **2,** 153 (1883).
[44] Larguier des Bancels: Compt. rend., **138,** 898 (1904).
[45] Barrett and Harris: Zeit. Elekt., **18,** 221 (1912).
[46] Engelmann: Arch. Neerland, **9,** 332 (1874).

trification[47] appear to have been confirmed by an unique experiment known as the Bose-Guillaume phenomenon.[48] If two wires, one of which is coated with porous material such as gelatin, be placed in a solution and the coated wire given a sudden twist, a momentary E. M. F. is produced, which is detectable with a ballistic galvanometer. This phenomenon may be interpreted as an enforced osmotic effect, in which liquid is momentarily squeezed out of the pores of the wire coating, and since the liquid is charged by contact oppositely to the coating itself, a very brief separation of charges occurs. This gives rise to a potential difference.

Girard was convinced from his work that the sign of charge on the membrane regulated the amount of solute diffusing through into the solvent. The correctness of many of Girard's conclusions are rendered somewhat doubtful by the careful studies of Hamburger.[49] Hamburger first showed that partitioning off two solutions by a non-protein membrane such as collodion had no effect whatever on the contact potential of the two solutions. This was found to be the case with fairly concentrated solutions of HCl and $Ce(NO_3)_3$, materials furnishing ions already known to be highly effective in altering the charges on the majority of negative colloids. From this work it seems reasonable to conclude that extensive selective ionic adsorption, at least for collodion, is not probable. Hamburger further arrived at the conclusion that the magnitude of charge and the electrical orientation of the membrane had very little influence on the diffusion rate of salts. He also believed that the osmotic flow was in the direction demanded by the calculated diffusion potential of the salt, and also that the magnitude of osmose depended largely on the specific effect of the salt itself.

It has been observed by Bayliss[50] and McClendon[51] and

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[47] Perrin: Compt. rend., **147,** 55 (1908).
[48] Bose-Guillaume: Compt. rend., **147,** 53 (1908).
[49] Hamburger: Zeit. Physik. Chem., **92,** 385 (1917).
[50] Bayliss: Proc. Roy. Soc., **84B,** 245 (1911).
[51] McClendon: Physical Chemistry of Vital Phenomena, p. 113 (1917).

often in this laboratory that the potential across a membrane boundary increased rapidly to a maximum value and receeded again practically to zero, especially with the more concentrated solutions. With thicker membranes such as porcelain, the change was slower, but with thin membranes the effect was very rapid. Bayliss found the maxium value approximated that calculated from Nernst's formula. The rapid fall of the potential has been ascribed to swelling of the membrane and consequent enlargement of the pores. That this view is in error, is evident from the identical effect encountered with porcelain, the pore size of which, it must be admitted is constant.

Very recently Loeb [52] working with collodion membranes has made potential measurements of osmotic systems of so-called gelatin chloride solutions containing HCl and finds experimentally the same potential value as calculated from Nernst's formula on the basis of the hydrogen ion concentration; again demonstrating the E. M. F. measured to be concentration cell and contact potential.

Bartell and Hocker[53] working with porcelain, and Bartell and Madison[54] with gold beaters skin membranes came to the conclusion that osmosis of electrolytes was largely controlled by the same factors as those which are active in electro-osmose, namely a fall in potential along a membrane pore which influences the direction of migration of the electrically charged water layer within the capillary. They considered the source of this potential as due to general diffusion of solute, relative ionic migration velocities of the salt used, and selective ionic adsorption, the usual resultant being a combined effect of the three factors.

The usefulness of collodion as a membrane material was recognized in 1855 by Fick[55] who used it in his studies on diffusion. The ease with which dialyzing membranes can be pre-

[52] Loeb: J. Gen. Physiology, **3,** 557 (1921).
[53] Bartell and Hocker: J. Am. Chem. Soc., **38,** 1029, 1038 (1916).
[54] Bartell and Madison: J. Phys. Chem., **24,** 444, 593 (1920).
[55] Fick: Pogg. Ann., **94,** 59 (1855).

pared from collodion has resulted in its use by many biologists.

In 1907, Bigelow and Gemberling[56] found that Poiseuille's law for the flow of liquids through capillaries applied to collodion as also to several other osmotic membranes. Mathews[57] made a number of qualitative experiments with collodion as an osmotic membrane, and concluded that it was not a truly semipermeable membrane. He believed that the direction and magnitude of osmose was largely a question of solubility. More recently Loeb[58] has prepared sacs of collodion with which he has studied the influence of electrolytes on the electrification of the walls of the sacs and also has studied the rate of diffusion of water through them. He found that the rate of diffusion of water was influenced not only by the concentration, but also by the electrical forces. In nearly all of his experiments the collodion membrane was impregnated with gelatin and in this respect his membranes differed from those used in this investigation.

II. PURPOSE OF INVESTIGATION.

The work undertaken in this investigation may be classed under three heads.

1. The determination of the relationship between the osmose of a number of electrolytes and the electrical properties of the membrane system when collodion membranes are used.

2. The determination of the relationship between membrane pore size, osmose, and the rate of salt diffusion through the membrane.

3. The determination of the effect of continuous stirring of the solutions on the rate of osmose and also on the rate of salt diffusion.

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[56] Bigelow and Gemberling: J. Am. Chem. Soc., **29,** 1576 (1907).

[57] Mathews: J. Phys. Chem., **14,** 281 (1910).

[58] Loeb: Loc. cit.

III. RELATIONSHIP BETWEEN OSMOSE AND ELECTRICAL PROPERTIES OF MEMBRANE

Preparation of Membrane

The preparation of collodion sacs for dialysis has been undertaken by many investigators, among whom Novy[59] seems to have been the first to have developed a satisfactory and simple technique that yields sacs similar in properties. Loeb[60] has used collodion membranes which were formed on the inside of a 50 cc Erlenmeyer flask, then subsequently removed after drying and wetting with water. It was found by us that this method yielded sacs of varying permeability and thickness, also that different portions of the same sac varied considerably in these respects.

Preliminary work with these sac membranes revealed the fact that to prevent the partial collapse of the sac, when the filled sac with its manometer tube was lowered into a dish of water, the experiments must be started under an hydrostatic head, which in itself is undesirable for the experiment. Even under an hydrostatic head of 20–40 mm, small wrinkles in the sac were not eliminated, and one to five minutes were necessary before the sac was filled sufficiently to register osmose on the manometer. Results obtained by us showed conclusively that a sac the shape of which was not maintained rigidly would stretch badly, and in the case of materials giving a strong osmose, one such sac was found to have stretched so that the initial sac volume was increased by 8 cc which represents approximately 15% change in total volume and an even greater percent error in osmose readings. The first problem then was to prepare uniform membranes of any required permeability and thickness, and of such shape that they could be held rigidly in place in the osmotic cell.

The method of Bigelow and Gemberling[56] for casting uni-

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[59] Novy: J. Am. Chem. Soc., **29**, 1578 (1907).

[60] Loeb: J. Gen. Physiology., **1**, 717 (1919); **2**, 87, 173 (1919); **2**, 387, 659, 673 (1920).

form flat membranes on a mercury surface was found to yield excellent results. To obtain membranes with similar properties it was found necessary to control the whole casting and drying process within a closed box. This was done in order to avoid uneven air currents and also to keep the temperature constant.

The following procedure was found to give membranes of any desired permeability in sheets 12 x 18 inches and of uniform thickness. 100 cc of 3 percent soluble gun cotton, dissolved in a mixture of 75 percent ether and 25 percent alcohol, was diluted with an equal volume of solvent to reduce its viscosity. This solution was poured evenly over clean mercury in a shallow pan placed within the casting box and allowed to evaporate slowly. At 25° C the casting time was about four hours for a membrane of medium permeability. A shorter drying period yielded more permeable, and a longer drying period or higher temperatures, less permeable membranes. The permeability was also affected by varying the proportion of water in the alcohol-ether diluent. The perfectly clear, colorless membrane was cut away from the sides of the casting dish with a razor blade, and turned the other side up for 15 to 20 minutes. The air was then changed in the casting box and the membrane turned over several times at short intervals. Very permeable membranes at this juncture began to appear opalescent, while the less permeable did not alter in appearance. The membranes were then immersed in water to dissolve out the remaining ether and alcohol.

Bigelow and Gemberling have shown that the permeability of membranes prepared in a somewhat similar manner, increased gradually for about a month, after which the change was slight. With a view to shortening the curing period, the effect of soaking the membrane in varying concentrations of alcohol and water, as suggested by Brown[61] was tried. Such curing weakened the membranes so materially that this method was abandoned, and curing in distilled water which

[61] Brown: Biochem. J., **9**, 320, 591 (1915).

was changed daily for thirty days was adopted as the most satisfactory procedure. All of the membranes were then cut with a cork borer, so as to fit the osmose cell, and stored under water until used. The marginal inch from the large cast sheet, by which the latter had been handled during the drying and curing periods was discarded.

Construction and Assembly of Osmose Cell

The double-compartment osmose cell of the type used by Bartell and Hocker,[53] and later by Bartell and Madison,[54] was used and has proved satisfactory. This cell possesses certain desirable points, such as ease of detection of leakage, elimination of evaporation, elimination of alteration of hydrostatic pressure due to temperature fluctuation, negligible capillary corrections, comparative simplicity and general ease of operation.

As the membrane used in this research possessed neither the rigidity of porcelain, which could be wired into place, nor the flexibility of gold-beaters skin, which could be waxed into position, and furthermore, had to be kept moist constantly, a different type of holder was of necessity devised.

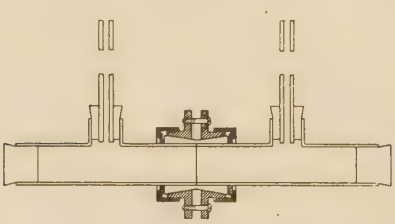

Fig. 1

The cell used in this work (Fig. 1) was constructed of two glass T-tubes of 15 mm diameter, each of which was fitted into a rubber stopper. These were fitted in turn into a threaded brass collar which carried on one end a circular brass plate. The stopper was held in the collar by a washer secured by a threaded sleeve which could be screwed onto the collar. The half-cells were bolted together through the circular brass plates. Paraffined rubber stoppers were used to close the ends of the cell and also as connectors for the osmometer tubes. The assembled cell was made fast to a substantial support.

In assembling the cell, the glass T-tube was adjusted

so that the surface of the rubber stopper on which the membrane was to be placed, projected slightly beyond the glass so that when the two halves of the cell were bolted together, the glass T-tube would practically touch the membrane. This definitely established the effective membrane area. In order to exclude the possibility of loss of liquid from either compartment of the cell by leakage around the edge of the membrane, the faces of the rubber stoppers were coated with three layers of rubber cement, the first two layers thoroughly dried with the long axis of the cell in a vertical position, and the third coat dried to the "gummy" stage. The membrane which had previously been cut out with a cork borer, was removed by forceps from the water under which it had been stored. It was then dried superficially with filter paper, placed in position on the prepared stopper, and the other half of the cell was bolted on. The bolts were taken up slowly and uniformly so as to avoid buckling of the membrane. The cell was then filled with water and left for at least twenty-four hours before being used. The volume of each compartment was approximately 20 cc.

The osmometer tubes were heavy-walled glass tubing of 2.5 mm internal diameter and were calibrated in the usual manner with mercury. The tubes used in the first part of this work agreed in specific volume to within about five percent, and were of fairly uniform diameter throughout. A given pair of tubes was always used with the same cell.

In setting up a cell for use, the water was first emptied out and the respective compartments rinsed twice with the solutions they were to contain. The compartments were then filled, and the osmometer tubes, previously half filled, were adjusted so that the liquid columns were equal. The rubber stoppers were then immediately waxed into place. In this work, readings of the hydrostatic pressures which developed were taken at two hour intervals over a twelve hour period. At the close of the experiment the cell was emptied, washed with distilled water, and then filled with the water. In order to wash the membrane capillaries free from electrolyte, the cell was put under an hydrostatic head for eight to ten

hours. In this way one membrane could be used a number of times, and still give results comparable with a fresh membrane. Results with the two-compartment cell, when the temperature was accurately controlled, were readily duplicable to within one or two percent.

What was actually obtained in this work was data showing the rate of flow of solutions through the membrane. In some cases the equilibrium pressure of the solution (expressed in terms of hydrostatic pressure) was determined; that is, readings were recorded when the rate of flow of liquid through the membrane in one direction was just balanced by the rate of flow in the other direction. Such readings will be designated as maximum osmose values. It will be appreciated that the comparison of the rates of flow of different solutions is by no means an exact way of comparing the absolute osmotic activity of the solutions. It does, however, give us a fairly accurate indication of the order of maximum equilibrium pressures obtainable with these solutions.

Results were obtained (1) with chlorides of metals having different valencies, (2) with potassium salts having inorganic acid radicals of different valencies, (3) with potassium salts having organic acid radicals of different valencies and (4) with hydrochloric acid and with potassium hydroxide.

The results obtained are shown in Table I. In this table readings obtained at the end of the two hour, six hour, and twelve hour periods are given. A medium porous membrane (pore diameter = 0.8 to 0.9 micron) was used. The salts were usually recrystallized twice from a good grade of distilled water. The HCl was redistilled as "constant boiling" from C. P. acid. The KOH was a Kahlbaum product and was freed from carbonate by careful precipitation with $Ba(OH)_2$. There was a slight trace of barium left in the solution. Stock solutions of the electrolytes were made up with conductivity water, analyzed, and diluted to the desired concentration. Conductivity water was used in one compartment of the cell in all experiments. The hydrostatic pressure was recorded in millimeters. The temperature was 25° C ± 0.5° C.

Osmose of Solutions of Chlorides of Different Metals

Chlorides of monovalent metals gave a repressed effect at 0.1M concentration. This effect persisted throughout the entire 12 hour period.

Solutions of chlorides of bivalent and trivalent metals at low concentrations (0.01 to 0.1M) tended to give either a low positive or negative osmose, while the osmose was strongly positive at higher concentrations (1M).

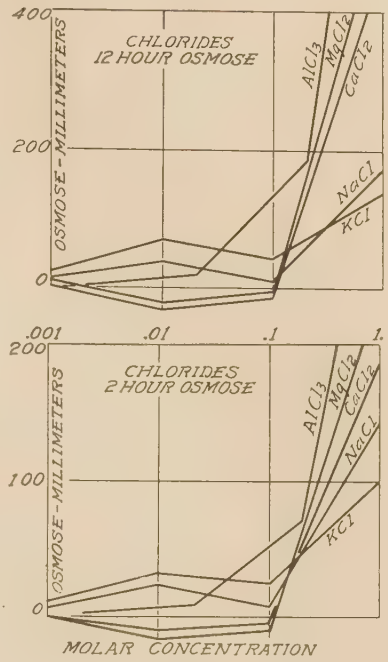

Fig. 2

The general shape of the curve representing initial osmose rate, (i. e., osmose in mm at the end of a two hour period), plotted against the logarithm of molar concentration, is the same in all cases as the maximum osmose curve (12 hour period) plotted in the same manner. These curves are shown in Fig. 2. The data appear in Table I.

Osmose of Solutions of Potassium Salts of Inorganic Acids

These experiments were carried out to ascertain the effect of the valence of the anion on osmose. It was found that an increase in valence of anion (with salts which do not hydrolyze greatly) resulted in an increase of the initial osmose rate and also in a higher maximum osmose value.

In concentrated solutions, readily hydrolyzable salts of inorganic acids (i. e., carbonate, phosphate, etc.) when compared with slightly hydrolyzable salts of inorganic acids of equal anion valence, were found to give an abnormally high osmose. In dilute solutions, the readily hydrolyzable salts

TABLE I

Osmose of Salt Solutions
(Values are given in millimeters)

Salt	2 Hr. Period Concentration				6 Hr. Period Concentration				12 Hr. Period Concentration			
	0.001M	0.01M	0.1M	1M	0.001M	0.01M	0.1M	1M	0.001M	0.01M	0.1M	1M
KCl	10	31	24.5	100	15.5	60	41.5	165	20	67	41.5	149
NaCl	7	24.5	5	146	11.5	43	6.5	227	13	38	4.8	183
$CaCl_2$	2	− 6.5	−2.5	188	4	−16.5	− 2.5	388	3	−21	−2	477
$MgCl_2$	1.5	−13	−5.5	240	3.5	−28.5	−14	521	4	−36	−14	654
$AlCl_3$*	0.0	10.5	73.5	367	0.0	22	156	805	0.0	27	190	1045
K_2SO_4	37	62	66	196	90	137	132	391	129	165	142	425**
$K_3FeC_6N_6$	61	103	109	276	146.5	228	205	547	220	269	222	590**
$K_4FeC_6N_6$	83	123	156	405	204	282	322	829	305	350	376	943**
K_2CO_3	26	247	375	410	61	590	697	900	81.5	760	670	1036
K_3PO_4	27.5	88	98	422	63.5	219	209	945	102	291	247	1045
$KC_2H_3O_2$	12	57	61	179	21.5	127	119	352	31.5	198	130	385
$K_2C_2O_4$	21	106	86	362	63	232	174	750	103	291	196	830
$K_3C_6H_5O_7$	37	129	145	465	91	319	317	1100	151	455	404	1550
HCl	16	13.5	29	108	28	36	49	170	28	45	50	154
KOH	5	39	6.5	−11	10.5	81	17	—	16	92	17	—

* Concentrations of $AlCl_3$ were 0.002 M, 0.02M, 0.2M and M.

** Solution of 0.5M concentration was used in this case instead of 1M.

were found to give a somewhat lesser osmose than the slightly hydrolyzable salts.

When osmose is plotted against logarithm of molar concentration, the shape of the initial osmose curves is shown to be somewhat different from the maximum osmose curves. The initial osmose curve approaches a straight line. When taken over a longer time interval, the osmose curve is found to have developed into the peculiar N shaped curve having a minimum at 0.1M, as shown in Fig. 3.

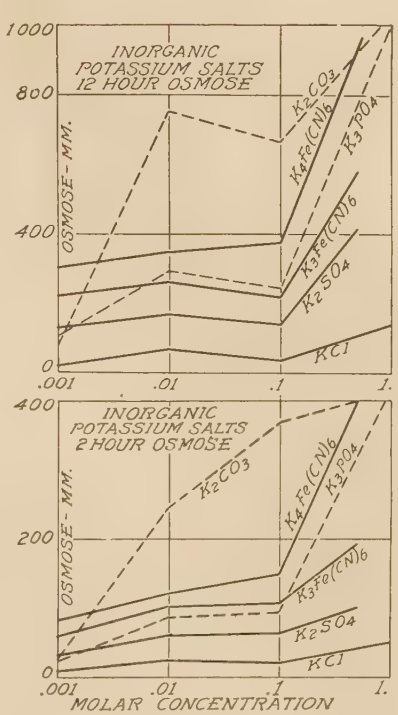

Fig. 3

Osmose of Solutions of Potassium Salts of Organic Acids

With increasing valence of anion, the osmose of salts of organic acids was found to increase in the same manner as did the osmose of salts of inorganic acids. (Fig. 4.)

The magnitude of the osmose of potassium salts of organic acids was greater at all concentrations than of the salts of inorganic acids, (i. e., slightly or non-hydrolyzable salts) of corresponding anion valence. (An exception is to be noted in the case of $K_2C_2O_4$ at 0.001M concentration, which gives lesser osmose but of the same order of magnitude, than the corresponding concentration of K_2SO_4.)

The initial osmose curve and the maximum osmose curve for $K_2C_2O_4$ when plotted against log. of concentration are both of the same shape and are of the N type.

The initial osmose curves for both acetate and citrate

show but little of the repression tendency; with time, osmose is repressed and these curves change to the N shaped type. In this respect, a close resemblance is noted between the behavior of the potassium salts of organic acids and the salts of inorganic acids.

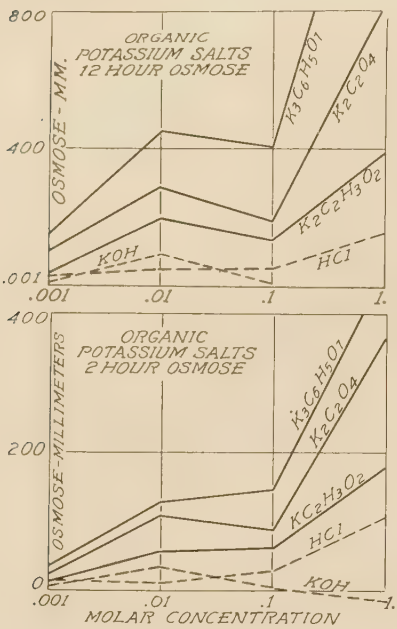

Fig. 4

Osmose of Solutions of Hydrochloric Acid and of Sodium Hydroxide

Hydrochloric acid gives a low positive effect which gradually becomes more positive with increase in concentration.

Potassium hydroxide at first gives increased positive osmose with increasing concentration, but in concentration greater than 0.01M, it shows a fairly strong negative tendency. At somewhat higher concentrations, the membrane becomes rapidly disintegrated; were it not for this fact we might, reasoning from our experience with other types of membranes, expect positive osmose with still higher concentrations.

Cell Potential

It was hoped that measurement of the development and subsequent decline in cell potential might be accomplished while osmose was actually taking place under the usual conditions. When calomel electrodes are used, in order to have the hydrostatic pressure register in the manometer and not continually leak out around the glass stop-cock on the calomel electrode, a perfectly fitting valve must be used. Unfortunately, there is practically no conduction through such a valve

when it is closed. This difficulty terminated temporarily the thought of measuring E.M.F. and osmose on the same experiment.

The potential measurements were made by the compensation method as described in a previous paper,[53] using calomel electrodes, a Leeds and Northrup precision potentiometer and a sensitive galvanometer. The solution side of the membrane is

TABLE II
Cell Potential
Potential Measured in Volts Temperature 25° C

Electrolyte	Concentration of Electrolytes			
	0.001M	0.01M	0.1M	1M
KCl	0	0	−0.005	−0.003
NaCl	0.0	0.008	0.019	0.030
$CaCl_2$	0.032	0.042	0.060	0.078
$MgCl_2$	0.034	0.050	0.065	0.085
$AlCl_3$*	0.032	0.052	0.076	0.087
K_2SO_4	−0.031	−0.028	−0.055	−0.072**
$K_3FeC_6N_6$	−0.025	−0.036	−0.059	−0.094**
$K_4FeC_6N_6$	−0.037	−0.050	−0.069	−0.097**
K_2CO_3	−0.017	−0.020	−0.030	−0.041
K_3PO_4	−0.030	−0.048	−0.064	−0.095
$KC_2H_3O_2$	−0.008	−0.029	−0.044	−0.052
$K_2C_2O_4$	−0.026	−0.040	−0.051	−0.078
$K_3C_6H_5O_7$	−0.042	−0.053	−0.075	−0.104
HCl	−0.035	−0.062	−0.109	−0.157
KOH	−0.010	0.032	0.068	0.081

* Concentrations of $AlCl_3$ were 0.002, 0.02, 0.2 and 1M.
** Solution of 0.5M concentration used in this case instead of 1M.

understood to have a higher potential than the water side when the sign is plus and a lower potential when the sign is minus.

The reversal of the electrical orientation of the cell system with increase in concentration of KOH appears to be unique, in these experiments and is the same condition noticed by Bartell and Hocker when using porcelain membranes with NaOH. With collodion, however, this reversal occurs at a greater dilution than with porcelain.

The electrical orientation appears to be controlled largely by the relative migration velocity of the respective ions in the solution, and is a function of the concentration as is demanded by Nernst's formula. So far as data on ionic velocities are available, they are found to agree with the expected direction and magnitude of cell orientation, with the exception of KOH in dilute solution, and with K_2CO_3. As the latter is fairly well hydrolyzed, we may expect a counter potential to be set up by the KOH produced, which would account for the low value actually found.

Sign of the Membrane Charge

It is possible to determine the sign of the membrane charge by either one of two methods, namely by electro-osmose or cataphoresis.

The use of gassing electrodes in electro-osmose experiments was clearly out of the question for any refined work. Electrodes such as those developed by Barratt and Harris[45] (i. e., Cu in saturated $CuSO_4$ solution) eliminate gassing and are excellent, but cannot be used in certain combinations such as ferrocyanides. Although a great deal of work was done with collodion membranes with a modification of Barratt and Harris' apparatus, and also by Briggs' method,[62] the cataphoresis method was found to be more satisfactory, since it was dependable and at the same time more rapid.

A quantity of dried membrane was finely pulverized, after which a fairly stable water suspension of it was made. This suspension was examined under the ultra microscope, and the direction of migration of the collodion particles under an applied potential noted.

The direction of motion of finely divided collodion particles in water was found to be slowly to the anode which indicated that collodion bears a small negative electrical charge with respect to water. In all four dilutions of each of the fifteen electrolytes tried, the collodion was likewise neg-

[62] Briggs: Jour. Phys. Chem., **22,** 256 (1918).

ative. It also appears that no amount of acid up to and including 10M HCl will cause it to become charged positively, nor will any concentration of salts of trivalent cation, such as aluminum, produce this effect. This appears to be an extreme case of an "unprecipitable" suspension. These results confirm those of Loeb and also those of Gyemant,[63] which were obtained by the electro-osmose method. In this respect collodion is different from any other membrane we have used.

General Discussion and Conclusions

It will be seen from the data already presented that the membrane charge and the orientation of the cell systems for chlorides of Na, Ca, Mg and Al are given according to B of Fig. 5.

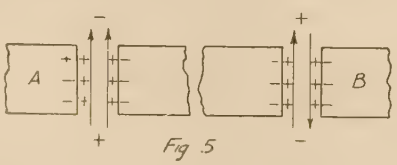

Fig. 5

The diagram represents one pore through the membrane. The solution side is understood to be above the membrane and the water beneath. The arrow on the left, pointing up toward the solution, represents the normal osmotic tendency while the one on the right represents the imposed electrical effect. Applying this idea we see that the exosmotic tendency opposes the normal osmotic tendency and we should expect a low degree of positive osmose (Na, Al) or even a negative osmose, which is actually realized with the case of Ca and Mg. At high concentrations, the normal osmotic tendency overcomes the imposed exosmotic effect, and positive osmose results.

The condition with HCl (also with KCl) is shown in A of Fig. 5, the orientation being the opposite of that in the above case. The osmotic tendencies should operate in the same direction and a high positive osmose should result. While in dilute solutions of HCl, positive osmose is obtained which is of greater magnitude than with Na, Ca, Mg, and Al, these latter substances in concentrated solutions give an osmose

[63] Gyemant: Kolloid Zeit., **28,** 103 (1921).

which materially exceeds that with HCl. It might be argued, though admittedly not at all conclusively, that except in the case of NaCl, this is due to the greater number of ionic units furnished by the dissociation of the more complex salts.

The peculiar case of KOH with its reversal of orientation with change of concentration, is an admirable illustration of the applicability of the electrical theory. In dilute solutions, the condition of the system is such that a strong positive tendency should result. (A, of Fig. 5.) The results are in accord with this prediction. In a more concentrated solution, however, the orientation changes and conditions are as in B, giving a weak positive effect; with still higher concentrations, a strong negative effect results.

All the potassium salts studied gave orientations of the cell system corresponding to A, Fig. 5, which would lead us to infer that abnormally positive osmose should result. This has been shown to be true (with the exception of $K_2C_2O_4$) so far as initial osmose rate is concerned. The maximum osmose, however, shows that some factor, of which time is an important element, plays a part in reducing the initial high osmose rate to a considerably lower value.

Summary and Conclusions

1. A method for preparing flat collodion membranes of uniform thickness and permeability is described. Methods for controlling the permeability to any desired value are given.

2. A non-leaking osmotic cell of two T-shaped glass compartments of equal volume, held together by a machined brass coupling which also holds the membrane firmly between the two compartments, has been developed and used successfully.

3. The osmose values obtained with thirteen different salts, an acid and a base (chosen to show the relative influence of cation and anion valence, hydrolyzability of salt, and weak and strong acid radical) are given for 0.001, 0.01, 0.1, and 1M concentrations.

4. The maximum potential of each of these osmotic systems was measured and recorded.

5. The sign of the membrane charge has been determined by cataphoresis, using finely ground membrane material in suspension.

6. Consideration of the data obtained shows that the initial osmose rate of practically all the salts examined bears a definite relationship to the electrical properties of the membrane system.

7. The anomalous effects obtained with collodion are very similar to those obtained with membranes of porcelain, of gold beater's skin, of calf's bladder, and of parchment paper. The maximal and minimal values obtained with these different membranes do not come at exactly the same concentrations, but when consideration is given to the exact condition of the electrical orientations of the different membrane systems, the results are closely comparable.

8. It has been shown that anomalous effects are related somewhat to the time factor. For example the data for the osmose of potassium carbonate at the end of a two hour period, when plotted against log of concentration of potassium carbonate gave no N shaped curve while the N shape was pronounced for the curve obtained at the end of a 12 hour osmose period. This fact makes it appear probable that the process of diffusion is in some way responsible for the repressing effects noted at the intermediate concentrations.

IV. RELATIONSHIP BETWEEN MEMBRANE PORE SIZE, OSMOSE AND RATE OF SALT DIFFUSION THROUGH THE MEMBRANE

In the foregoing section of the thesis, it was shown that the direction and magnitude of initial osmose of solutions of a large number of salts, also of acid and alkali, with collodion membranes were in accord with the anomalous osmose theory

as previously outlined by Bartell and co-workers.[53,54,64] In the section above referred to, attention was called to the change in shape of the osmose rate curve with time. A so-called straight line curve was obtained when the initial osmose values (two hour osmose readings) were plotted against the concentration, while a peculiar N shaped curve was obtained when the maximum osmose values (i. e., obtained after 12 hours or more) were plotted against concentration. The latter exhibited a minimum point at about 0.1 M concentration.

From the fact that the straight line initial osmose rate-concentration curve developed into the N shaped curve with time as the only apparent influencing factor, it was inferred that diffusion of electrolyte was the active factor directly responsible for the decided alteration of osmose rate through this concentration range.

In order to test this idea, collodion membranes of different degrees of permeability were prepared in the manner described in the previous paper. The number of capillary holes through a given area of membrane will be shown to be nearly the same in all cases. The actual diameter of the capillaries was regulated at the time of setting and by the amount of evaporation of solvent which occurred before soaking in water.

Permeability of the Membranes

The permeability of the membranes used in this work was determined by the hydrostatic method of Bigelow and Gemberling.[56] A known and constant hydrostatic pressure was applied to water in contact with the membrane and the rate of passage of water through the membrane accurately noted on a calibrated capillary tube by means of a cathetometer. The cells were sealed with wax around the rubber stoppers, so that leakage was eliminated. They were then immersed in a thermostat. An idea of the reproducibility of the collodion membranes and the constancy of the effective membrane areas of the various cells may be gathered from the close agree-

[64] Bartell and Sims: J. Am. Chem. Soc., **44**, 289 (1922).

TABLE III

Membrane Permeability (Very Permeable Membrane)

Membrane no.	Pressure applied, mm H_2O	Water passed, cu. mm	Time, sec.	Cu. mm $\times 10^{-4}$ water passing per sec. per sq. cm diaph. area
1	385	18.48	337	319
2	385	19.50	355	319.3
3	385	23.16	421	320
4	385	18.90	344	319.5
Average				319.45

Diaphragm Area = 171.2 sq. mm. Temperature = 20° C

TABLE IV

Relative Membrane Permeability

Temperature = 20° C

Pressure applied, mm H_2O	Cu. mm $\times 10^{-4}$ water passing per sec. per sq. cm. dia. area	Cu. mm $\times 10^{-4}$ water passing per sec. per sq. cm. area per mm pressure	Relative permeability
Least permeable membrane			
485	54.76	0.1129	
385	42.93	0.1115	
285	31.84	0.1117	
185	21.37	0.1155	
Ave.		0.1129	1
Medium permeable membrane			
492	109.32	0.2221	
392	87.82	0.2240	
292	64.84	0.2220	
192	43.29	0.2255	
		0.2234	1.978
Very permeable membrane			
485	403.10	0.8311	
385	319.45	0.8297	
285	236.20	0.8288	
190	158.08	0.8320	
		0.8304	7.355

ment of the results. Absolute results involving correction for viscosity of water at 20° C were not attempted, as comparative data at the one temperature were all that was desired to establish relative permeability.

The preceding table was compiled from average values obtained in the same manner as shown in the foregoing table.

From Poiseuille's Law for the flow of liquids through capillary tubes, we have the expression $Q = \frac{KnPD^4T}{L}$. Q represents the quantity of liquid passing through n, number of capillaries of diameter D and length L, in the time T, and under pressure P. K is a constant, the value of which is dependent upon the liquid used, the temperature, etc. It is assumed that the length of the capillary pore in the various membranes is a function of the thickness of the membrane. Under the conditions of the experiment, K, P, and T may be combined into a single constant k and the equation rewritten $Q = \frac{knD^4}{L}$. If we assume for the time being that n is a constant for all three membranes, we are able to compare the relative pore diameters of the membranes.

The actual thicknesses of the three membranes were, respectively, 0.08 mm, 0.15 mm, and 0.31 mm.

The relative diameters of the pores of the three membranes, calculated as above, give the values 1 : 1.38 : 2.31.

Measurement of Membrane Pore Size

The membrane pore size was measured directly by the method, based on Jurin's Law, as used by Bigelow and Bartell.[15] This gives us information relative to the assumption made concerning the number of pores in each of the membranes used. In case the relative pore diameters as measured by the two independent methods agree, we are justified in the previous assumption that the number of pores in a given area of membrane is the same for all three membranes.

The membrane was supported in a holder by a fine-mesh

wire screen. Owing to the nature of the membrane, which was somewhat elastic, and which stretched under the pressure necessary to force water out of the pores, the values here reported must be considered as representing pores which have been slightly stretched. Results obtained follow:

TABLE V
Membrane Pore Size

	K. Gms pressure per sq. cm.	Pore diameter, microns	Relative Pore Diameter	
			Jurin's Law	Poiseuille's Law
Least permeable membrane	4.23	0.701	1.00	1.00
Medium permeable membrane	3.17	0.934	1.33	1.38
Very permeable membrane	1.76	1.681	2.39	2.31

The above agreement between the values for relative pore diameter, as determined by the two different methods, indicates the validity of the assumption that the number of pores in a given cross-sectional area of the various membranes is very nearly the same, at least within 3 to 4%. We shall throughout this paper, distinguish between these three membranes by referring to them as (*a*) least permeable, (*b*) medium permeable, and (*c*) very permeable.

Osmose through Membranes of Different Degrees of Permeability

The validity of the hypothesis that diffusion was responsible for the change in shape of the osmose rate-concentration curve, may be tested by comparing the osmose through the membranes of different permeabilities. The membrane of least permeability should show an initial rate-concentration curve which approaches more nearly a straight line than do the curves obtained with the other membranes of greater permeability. The membrane of medium permeability should show less of the straight line effect, and should rapidly develop

the N type of curve, while the very permeable membrane should probably show no straight line effect at all, but should give instead the N shaped curve from the beginning.

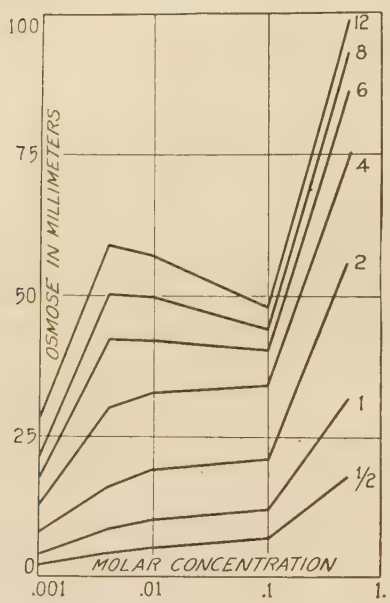

Fig. 6

Development of N shaped Osmose Curve as influenced by time in case of KCl. Least permeable membrane. Time in hours

In all of the work described in this paper, very carefully selected osmometer tubes of 2.5 mm internal bore were used. These were selected from among over four hundred tubes and the volumes of given lengths of them varied not more than one percent. This uniformity was considered satisfactory. The duplicability of osmose experiments with these refinements and with good temperature control was close to one percent.

Inasmuch as it was desired to obtain results when membranes of different permeabilities were used, both with representative potassium salts with anions of different valencies and with salts of bivalent and trivalent metals, the following were used: KCl, $CaCl_2$, $AlCl_3$, K_2SO_4, and $K_3FeC_6N_6$. In addition, sucrose was also used in order to ascertain how the osmose of a substance supposed to give a normal osmose rate was affected by permeability. One concentration in addition to those used in the previous work was introduced, namely, 0.004 M. The recession in the N shaped curve started to develop with potassium salts at about 0.004 M concentration. In place of 1 M concentration 0.5 M was substituted, the osmose in this region of concentration was of the positive type, and proved to be of no special import in this in-

vestigation. The hydrostatic pressure was read at thirty minute intervals for the first two hours, after which two hour readings were generally made. Close watch, however, was kept on the experiments as they neared the maximum, so that the extreme pressure developed would be known. The accompanying Table VI for KCl contains data such as was obtained for all solutions investigated. In order to economize space, only values read at the end of 2 hr., 12 hr., and at maximum

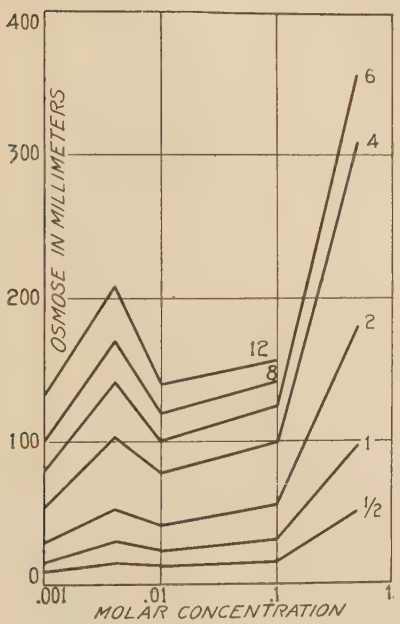

Fig. 7

Development of N shaped Osmose Curve as influenced by time in case of K_2SO_4. Least permeable membrane. Time in hours

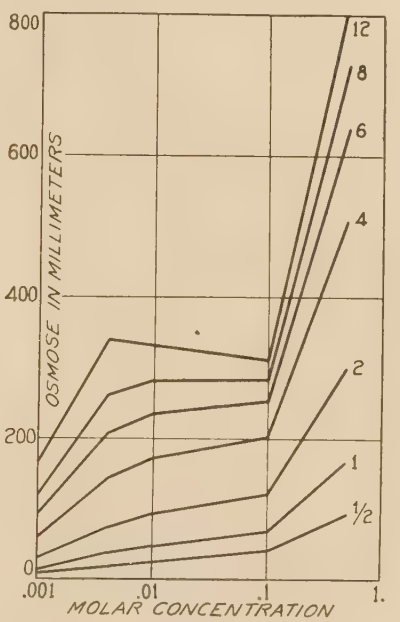

Fig. 8

Development of N shaped Osmose Curve as influenced by time in case of $K_3Fe(CN)_6$. Least permeable membrane. Time in hours

osmose will be given. The development of the N shaped curve with time is shown for potassium salts in Figures 6, 7, and 8, the time being expressed in hours. The effect of increasing the membrane pore diameter on the initial osmose rate-concentration curve is shown in Figures 9, 10, and 11.

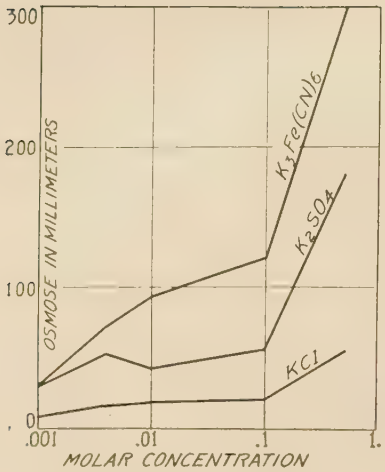

Fig. 9

Initial Osmose Rate (2 Hrs) of Potassium Salts.
With least permeable membrane

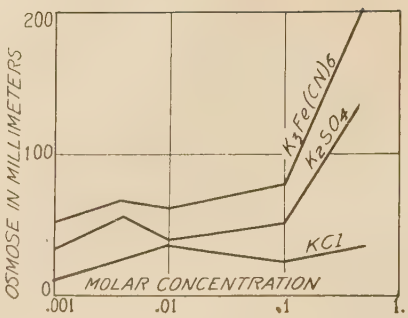

Fig. 10

Initial Osmose Rate (2 Hrs) of Potassium Salts.
With medium permeable membrane

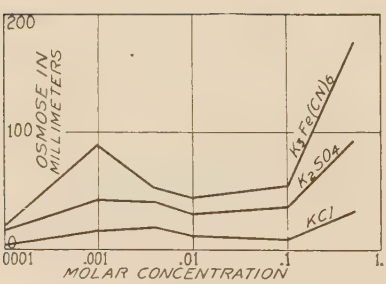

Fig. 11

Initial Osmose Rate (2 Hrs) of Potassium Salts.
With very permeable membrane

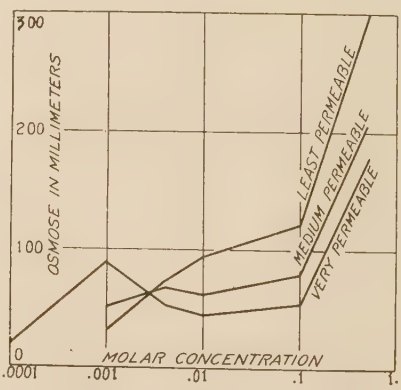

Fig. 12

Initial Osmose Rate (2 Hrs) of $K_3Fe(CN)_6$
With membranes of different permeabilities

Figure 12 shows the initial (2 hr.) osmose rate-concentration curve for $K_3FeC_6N_6$ with all three membranes.

TABLE VI

Osmose of KCl (Least Permeable Membrane)

Osmose period, hrs.	0.001 M	0.004 M	0.01 M	0.1 M	0.5 M
0.5	2	4	4	7	18
1	4	8.5	10	12	32
1.5	6	12	15	16.5	44.5
2	8	16	19	21	56
4	13	30	33	34	74
6	17.5	42	42.2	40	86
8	21.5	50	49.5	44	93
10	25	55	54.5	46.5	98
12	28.5	59	57	48	98
14	28.5	62	—	49.5	—
16	—	—	59	—	—
18	—	67	—	—	—
20	—	—	59	—	—
22	—	67	—	—	—

Summary

The following generalizations may be drawn from the foregoing data:

1. The *least permeable membranes*, i. e., the ones with pore diameters less than 0.7 microns, during the first five hours showed a tendency to give only positive osmose with all the salts used with the exception of $CaCl_2$, which gave a negative osmose. At no time during the first few hours did the N shaped curve become pronounced. (K_2SO_4 solutions gave a slight N shape with this membrane.) These facts indicate that the phenomenon of negative osmose is not entirely dependent upon the specific salt used, neither is it dependent entirely upon concentration, but its appearance is dependent also, and to a large degree, upon the diameter of the membrane pores. It seems probable that negative osmose does not occur until the diameter of the membrane pore reaches a certain limiting value, which is definite for a given salt solution. In this work we have noted that when negative tendencies pre-

TABLE VII

Osmose Values in Millimeters at the End of 2 Hr. and 12 Hr. Periods with Membranes of Different Permeabilities

Salt	2 Hr. Period Concentration					12 Hr. Period Concentration				
Least permeable membrane	0.001 M	0.004 M	0.01 M	0.1 M	0.5 M	0.001 M	0.004 M	0.01 M	0.1 M	0.5 M
KCl	8	16	19	21	56	28.5	59	57	48	98
$CaCl_2$	1.5	−2	−3	6.8	83	7.3	−2	−11	24	262
$AlCl_3$*	5	20.5	36.5	112.5	562	16	80	133.5	378	—
K_2SO_4	30	53	42	56	180	133	208	140	158	—
$K_3Fe(CN)_6$	32	73	94.5	122	300	166	339	331	311	806
Sucrose	—	0	1	21.2	106	—	.5	8.2	97.5	500
Medium permeable membrane										
KCl	11.2	26	36	23.5	35	37.2	94	120	55	75
$CaCl_2$	5	−2	−9	−6	53	15.5	−4.5	−25.8	−17.8	170
$AlCl_3$*	12	2	9.5	68	362	25	7	27	180	1004
K_2SO_4	33	56	40.2	51	140	142	210	136	136.2	400
$K_3Fe(CN)_6$	52	67	62	79	206	240	279	206	195	496
Sucrose	0	—	4	25	106	0	—	9	86	407
Very permeable membrane										
KCl	15.5	20	12.2	8.5	32.5	28.5	38	22	14	47
$CaCl_2$	0	−9	−14.5	−5.5	56.2	0	−15.5	−23	−7.2	88.2
$AlCl_3$*	4	3	8	59	285	7	4	12	96.5	554
K_2SO_4	42	41.5	31	36.5	92	71	60.5	39	43	119
$K_3Fe(CN)_6$	88.5	52.5	44	54	174	145	85	56	73	—
Sucrose	—	—	0	16	118	—	—	0.5	30	196

*Concentrations for $AlCl_3$ were as follows: 0.002 M, 0.008 M, 0.02 M, 0.2 M, 1 M.

TABLE VIII

Maximum Osmose Values obtained with Salt Solutions of Different Concentrations with Membranes of Different Permeabilities

Salt	Concentration									
Least permeable membrane	0.001 M Time in hrs.	Osmose	0.004 M Time in hrs.	Osmose	0.01 M Time in hrs.	Osmose	0.1 M Time in hrs.	Osmose	0.5 M Time in hrs.	Osmose
KCl	12	28.5	18	67	16	59	14	49.5	12	98
$CaCl_2$	12	7.3	24	−2	20	−13.5	14	26.5	18	287
$AlCl_3$*	14	17.5	18	89	16	142	20	407	6	1210
K_2SO_4	28	185	18	236	16	150	16	161	6	355
$K_3Fe(CN)_6$	48	380	36	512	20	359	14	314	13	809
Sucrose	—	—	42	2	30	14	30	125	33	695
Medium permeable membrane										
KCl	16	39.5	20	105	14	123	12	55	12	75
$CaCl_2$	12	15.5	18	−5.5	16	−27.6	12	−17.8	16	176
$AlCl_3$*	10	25	18	9	12	27	12	180	14	1006
K_2SO_4	18	156	18	223	14	140	12	136.2	14	405
$K_3Fe(CN)_6$	16	260	18	297	12	206	12	195	12	496
Sucrose	24	0	—	—	12	9	24	90	24	463
Very permeable membrane										
KCl	8	30.5	8	41	6	22	6	14	6	47
$CaCl_2$	6	0	6	−15.5	6	−23	6	−7.2	6	88.2
$AlCl_3$*	10	8.5	8	4.5	6	12	6	96.5	8	586
K_2SO_4	6	71	6	60.5	4	40	4	44	4	120
$K_3Fe(CN)_6$	8	149	6	85	6	56	6	73	4	224
Sucrose	—	—	—	—	6	.5	8	33	8	205

* $AlCl_3$ concentrations were as follows: 0.002 M, 0.008 M, 0.02 M, 0.2 M, 1 M.

vail, the negative effects became greater as the pore diameters are increased.

2. With *medium permeable membranes* (pore diameters less than 0.9 microns), the N shaped curve was fairly pronounced, though not obtained throughout the entire period of osmose, with the potassium salt solutions, KCl, K_2SO_4 and $K_3FeC_6N_6$. The repression in the curve occurred between 0.004 M and 0.1 M concentration.

3. With *very porous membranes* (pore diameters less than 1.6 microns), the N shaped curve became pronounced and was maintained throughout the entire period of osmose, from the initial to the final reading.

4. It should be pointed out that the N shaped curve was obtained even with the slightly permeable membranes, provided the experiment was allowed to continue for a sufficient length of time before osmose readings were taken. When readings were made at the end of a twelve hour period, a repressing effect was noted with all three potassium salts, this repression occurred between the concentrations of 0.004 M and 0.1 M.

5. With the least permeable membranes, the initial osmose rate of the concentrated solutions was greater than that obtained when the very permeable membranes were used. On the other hand, the rather surprising observation was made that the initial osmose rate of dilute solutions was less with the least permeable membranes than with the very permeable membranes.

6. The time required to reach maximum osmose was less with the very permeable membranes than with the less permeable membranes. Also, the maximum osmose attained with potassium salts was progressively less with increasing membrane porosity (an exception in the case of KCl with medium permeable membranes is to be noted).

7. The range of concentration over which repression of osmose occurred was greater with very permeable membranes than with the less permeable membranes.

8. The osmose of a substance of supposedly normal os-

motic tendencies, such as sucrose, showed a decreasing maximum value as the porosity of the membrane was increased. No N shaped curve was obtained with sucrose solutions.

Diffusion of Solute into Water Compartment during Osmose

It has been known since dialyzers of collodion were first used by Fick[55] that they were permeable to crystalloids. For this reason, the exosmotic current during an osmose experiment must be of considerable magnitude. A study of the exosmotic current has received but little attention from recent investigators in osmosis.

The passage of solute into the water compartment may be regarded as taking place in some one or more of the following ways:

1. Filtration, the passage of solute through the membrane pores due to hydrostatic pressure.

2. Diffusion, the passage of solute particles through the membrane pores due to their own motion and according to Fick's Law, dependent largely on the salt, the concentration gradient and the temperature.

3. Dissolving of solute in the membrane material itself, the membrane then giving up solute to the water compartment according to the partition law.

4. Adsorption of solute from the contents of the solution compartment by the walls of the membrane capillary and then the subsequent giving off of solute by the membrane to the contents of the water compartment, in order that the adsorption process between membrane and water may come to equilibrium according to the partition law.

In the case of collodion, all of the factors may be active simultaneously, hence the question arose which of these factors are the predominating ones. That this was a very intricate problem can be seen from the fact that diffusion, solution, and adsorption are quite interdependent, also diffusion and filtration effects are not easily distinguishable from each other.

Effect of a Given Salt and of the Pore Diameter of Membrane on Exosmotic Current or Salt Diffusion

The collodion membranes of different degrees of porosity which had already been used in the foregoing osmotic studies were used in this work. In these stationary cells, the osmotic experiment was stopped at the end of two hours and the contents of the water compartment removed and analyzed. Then another identical experiment was started and allowed to

TABLE IX

Millimols of Salt which passed through Membranes of Different Permeability during Two Hour Osmose Period

Stationary Cells				
Salt	Millimols of salt which passed through			
	Initial molar conc. in salt compartment	Very permeable (pore diam. about 1.6 micron)	Med. permeable (pore diam. about 0.93 micron)	Least permeable (pore diam. about 0.7 micron)
$K_3FeC_6N_6$	0.004	0.0045	0.0020	0.00155
	0.01	0.0129	0.0096	0.0090
	0.1	0.175	0.169	0.164
K_2SO_4	0.004	0.00193	0.00345	0.0034
	0.01	0.01205	0.0109	0.0144
	0.1	0.1584	0.155	0.1803
KCl	0.004	0.0032	0.0018	0.0020
	0.01	0.0115	0.0112	0.0107
	0.1	0.219	0.190	0.207
$CaCl_2$	0.004	0.00396	0.00264	0.00275
	0.01	0.01385	0.00835	0.01225
	0.1	0.173	0.097	0.199
$AlCl_3$	0.008	0.0137	0.0098	0.00587
	0.02	0.0234	0.02736	0.0234
	0.2	0.311	0.311	0.282

run to its maximum value, and the contents of the water compartment analyzed as before, so that not only the initial rate (2 hour period) would be known, but also the total amount of electrolyte which diffused from the cell by exosmose during the maximum osmose period.

Analyses of KCl, $CaCl_2$ and $K_3FeC_6N_6$ solutions were

done volumetrically, the chlorides by Mohr's method[65] and the ferricyanide by Muller and Diefenthaler's method.[66] $AlCl_3$ and K_2SO_4 solutions were analyzed gravimetrically by evaporations and ignition; also by precipitation and ignition of $Al(OH)_3$ and $BaSO_4$, respectively.

TABLE X

Millimols of Salt which passed through Membranes of Different Permeability during Maximum Osmose Period

Stationary Cells				
Salt	Millimols of salts which passed through			
	Initial molar conc. in salt compartment	Very permeable	Medium permeable	Least permeable
$K_3FeC_6N_6$	0.001	0.0028	0.0037	0.0048
	0.004	0.0138	0.0163	0.0188
	0.01	0.0344	0.0431	0.0551
	0.1	0.434	0.529	0.665
	0.5	2.216	3.042	3.444
K_2SO_4	0.001	0.005	0.0025	0.0038
	0.004	0.016	0.022	0.0237
	0.01	0.036	0.055	0.073
	0.1	0.460	0.626	0.808
	0.5	2.450	3.467	1.964
KCl	0.001	trace	trace	0.0021
	0.004	0.0175	0.0235	0.0329
	0.01	0.0479	0.0641	0.0790
	0.1	0.610	0.688	0.836
	0.5	3.112	3.77	4.265
$CaCl_2$	0.001	0.0014	0.0010	0.0014
	0.004	0.0764	0.0241	0.0261
	0.01	0.0476	0.0647	0.0837
	0.1	0.520	0.565	0.682
	0.5	2.651	3.596	4.30
$AlCl_3$	0.002	0.0070	0.0070	0.0080
	0.008	0.0293	0.0311	0.0332
	0.02	0.0315	0.104	0.275
	0.2	——	1.010	1.582
	1.0	5.5	6.38	4.01

Direct comparison of the total amounts of salt which passed through the various membranes during the maximum

[65] Mohr: Zeit. anorg. Chem., **63,** 330 (1909).

[66] Muller and Diefenthaler: Ibid., **67,** 418 (1910).

osmose period was a difficult matter, inasmuch as the time period of reaching maximum osmose depended not only on the specific salt and its concentration, but also, and more particularly, on the membrane porosity. For this reason, the amount of salt which passed through the membrane in a given time, say in two hours, must be considered a fairer means of comparing actual diffusion rates. Even then, comparisons of the diffused salts will be subject to some error, especially when made between the less porous and the very porous membranes, since in a two hour period, the osmose will have progressed relatively further with the more porous membranes than with the less porous membranes. Since the time interval for maximum osmose is nearly the same with the two least permeable membranes, no appreciable error of the type above indicated will be probable when comparisons are made between them. Such comparisons will be more justifiable than when comparisons are made between the least permeable and the very permeable membranes.

Summary

The foregoing data brought out the following conclusions:

1. The rate at which $K_3FeC_6N_6$ and $AlCl_3$ passed through the membrane was increased at all concentrations as the pore diameter was increased. On the other hand, relative diffusion values of K_2SO_4 and $CaCl_2$ decreased materially as the pore diameter was increased. The diffusing rate of KCl remained about the same with the different membranes.

2. In dilute solutions K_2SO_4, $CaCl_2$ and $AlCl_3$ appeared to pass through the membrane at a relatively greater rate than the other salts.

3. Comparisons of the rate of passage of potassium salts through the *least porous membranes* (i. e., with pore diameters of about 0.7 microns) in the case of dilute solutions gave the following anion order $SO_4'' > Cl > FeC_6N_6'''$. For concentrated solutions the order for the least porous membrane was $Cl > SO_4'' > FeC_6N_6'''$. This latter order was the inverse of the order

of magnitude of maximum osmose. Comparison of the rates of passage of chlorides into the water compartment showed the cation order in dilute solution to be $Al > Ca > K$. Exactly the opposite order $K > Ca > Al$ was found for concentrated solutions. The order for magnitude of osmose with dilute solutions, bore no apparent relation to the cation diffusion order, however, the order of magnitude of osmose with concentrated solutions was the inverse of the cation diffusion order.

4. With *medium porous membranes* (i. e., with pore diameters of about 0.93 microns) the anion order for rate of diffusion of potassium salts from dilute solutions was $SO_4 > Cl > Fe(CN)_6'''$ and with concentrated solutions was $Cl > SO_4 > Fe(CN)_6'''$. This was again the inverse of the order of maximum osmose for concentrated solutions. The cation order for rate of diffusion was $Ca > K > Al$ in dilute solutions, and $Ca > Al > K$ in concentrated solutions.

5. For *very permeable membranes* (i. e., with pore diameters of about 1.6 microns), comparison of the amounts of potassium salts diffused during the period of maximum osmose, showed the anion order to be $Cl > SO_4 > Fe(CN)_6'''$ for both dilute and concentrated solutions. This order is the inverse of the order of maximum osmose. For chlorides, the cation order with the most porous membrane was $K > Ca > Al$ in both dilute and concentrated solutions. This order was the same as the maximum osmose order in very dilute solutions, but was the converse of the order of maximum osmose in concentrated solutions.

6. If the pore diameter of an unstretched membrane, i. e., one not subjected to the high pressures such as were used in measuring pore diameters, is as we believe, slightly less than the diameter as measured with the stretched membrane, these membranes then have pore diameters of just about the same magnitudes as the copper ferrocyanide membranes investigated by Bartell[67] which were on the border line between osmotic effect and no osmotic effect.

[67] Bartell: Jour. Phys. Chem., **16**, 318 (1912).

7. Tinker[18] made a microscopic study of copper ferrocyanide gels and found: "The structure seems to be that of a somewhat irregular network having a mesh of the order 0.5 to 1.0 microns. In this respect, it seems to be similar to most of the other ordinary gels, such as gelatine, silicic acid, etc., which have been examined with great thoroughness by Bütschli, Hardy, van Bemmelen, von Weimarn, Quincke, Zsigmondy, Pauli and others. There seems to be a general agreement at the present time that most gels consist of a lattice work system in which a solid or semi-solid phase encloses a more liquid phase." The results of this investigation tend to corroborate the above view. The lattice work of the collodion membrane may be formed in such a manner that the net work forms a mesh of the order 0.5 to 1.0 microns. If the liquid phase is replaced by water when the lattice work is of this order the lattice work remains unaltered for months even though constantly subjected to filtration tests.

8. The work described in this section has clearly brought out the fact that the pore diameter of an osmotic membrane is a highly important factor in determining the exact nature of osmose. Furthermore, it seems probable that the phenomena of anomalous osmose and the attending salt diffusion is governed largely by the precise pore diameter of the osmotic membrane.

V. EFFECT OF STIRRING SOLUTIONS DURING OSMOSIS

The experimental work described in this section of the thesis was undertaken to test further the hypothesis of the author that passage of solute through the membrane was largely responsible for the N shaped curves observed with collodion membranes. If this hypothesis is correct, we shall expect that even with the least permeable collodion membrane (pore diameter = 0.7 micron) the N shaped curve will be initially apparent in the case of potassium salts when the solutions are stirred. In

addition, we should expect a much greater positive osmose in the shaken cell with potassium salts giving the correct electrical orientation for abnormally positive osmose, for the reason that in the shaken cell, diffused solute should be rapidly removed from the face of the membrane on the water side, thereby maintaining a greater potential and concentration gradient across the membrane. In the cases of $CaCl_2$ and $AlCl_3$, salts giving an electrical orientation favorable to negative osmose, we shall expect a greater negative effect in the shaken than in the stationary cell. Diffusion of solute in the shaken cell may be so augmented by the effect of the continuous stirring that an N shaped osmose curve may also be observable with $AlCl_3$, which hitherto has shown no such tendency in our experiments with membranes of different pore size.

It has been shown by Kahlenberg[21] that the osmose rate is materially changed by stirring the solution in the cell. Cohen and Commelin[68] also report osmose experiments in which the solutions were stirred, but they could not duplicate their results. A decided change in osmose values has often been observed in this laboratory when the stationary osmose cells have been accidentally disturbed.

The contents of the osmose cell of the T-type was found to be stirred to uniform composition very quickly by placing a metal ball in each compartment, then rocking the entire cell slowly back and forth. This method of stirring possessed none of the mechanical difficulties such as are encountered when externally driven rotary stirrers are used. Changes in concentration in each compartment of the cell were noted by measuring the conductivity of the solutions.

Construction and Assembly of Rocking Cell

The construction of the cell, shown in Figure 13, was the same as used in our previous work with the exception of the introduction of two circular platinum electrodes, connections

[68] Cohen and Commelin: Zeit. phys. Chem., **64,** 1 (1908).

to which were made through glass inseals in each compartment. The inseal glass tubing was cut off at an appropriate length so as to serve as a mercury cup through which electrical contact with the outside of the cell could be established.

The cell was assembled in the usual manner. The platinizing of the electrodes and the washing was done in the usual way and before the membrane was put in place. The assembled cell was rinsed with several changes of water and then placed under an hydrostatic pressure to clean the membrane capillaries.

The conductivity constant for each chamber of the cell was determined before each pair of osmotic experiments

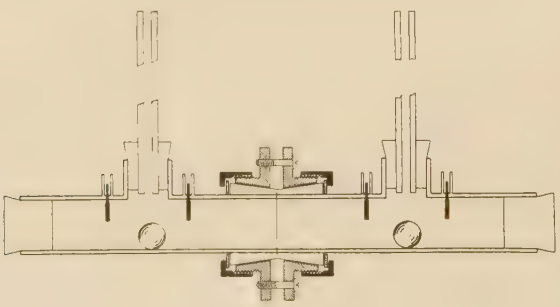

Fig. 13

Osmose Cell, Rocking Type with Electrodes

(M/50 KCl solution being used for this purpose). It was found that the specific conductance of the M/50 KCl at first changed gradually at constant temperature. This was traced to adsorption of KCl from the solution by the membrane. It was found necessary to allow the membrane to come to equilibrium with the KCl solution after which this solution was replaced with fresh KCl solution before the cell constant could be determined. This manipulation was found to yield reproduceable results. After the cell constant had been determined, the cell was rinsed with water several times, and then the hydrostatic pressure applied; finally the cell was again rinsed with conductivity water.

The Thermostat and Rocking Machine

The thermostat was a large air bath, approximately 2 x 4 x 6 feet high, electrically heated, and cooled by a large metal cold water coil. Rapid circulation of air was maintained by an electric fan. The temperature was $25° \pm 0.02°$ C. During operation the current in the heater was thrown off and on by a sensitive toluene regulator approximately every five seconds. Within the thermostat was an electric motor which through reducing gears drove the rocking platform, which carried the osmotic cell, at a slow and even rate. Uprights were attached to the platform, and carried between them a cross piece with narrow slots cut at the proper distance to support the osmometer tubes. Two coiled wire springs of equal tension were attached from the base of the apparatus to each side of the upright. This avoided any jerking motion of the rocking platform during operation.

The front and one side of the thermostat were of glass. The front was in two sections, the upper and lower halves of which could be raised or lowered as occasion required.

Method of Setting up Cell for Experiment

Previous to setting up the cell, the solutions and conductivity water to be used were allowed to come to the temperature of the thermostat. The long osmometer tubes were then half filled with solution or water, depending on the chambers with which they were to be used. Each compartment of the osmose cell was then rinsed twice with the solution it was to contain, filled with solution, air bubbles removed and a monel metal ball lowered into each compartment. The osmometer tubes were next inserted and adjusted to the same level. The apparatus was then fastened onto the rocking platform and the stoppers of the osmometer tubes waxed into place.

At the close of an experiment, the rocking machine was stopped, the cells taken out and the solutions and metal balls removed by taking out the stoppers in the two ends of the cell. The osmometer tubes were then removed and the cell washed in the usual manner.

TABLE XI

Osmose Values in Millimeters at the End of 2 Hr. and 12 Hr. Periods with a Rocking Cell

Salt	2 Hr. period					12 Hr. period				
Concentration	0.001 M	0.004 M	0.01 M	0.1 M	0.5 M	0.001 M	0.004 M	0.01 M	0.1 M	0.5 M
$K_3Fe(CN)_6$	49	101	85	98	290	232	408	263	264	755
K_2SO_4	29	60	53	45	146	170	283	187	143	470
KCl	14	33	35	23	52.5	48	91	83	48	113
$CaCl_2$	5	3	−7	17	98	13	3	−18	33	275
$AlCl_3$	3	15	22	99	412	9	72	89	316	1300
Sucrose	—	—	—	22	143	—	—	—	79	512

TABLE XII

Maximum Osmose Values obtained with Salt Solutions of Different Concentrations with Rocking Cell

Salt	0.001 M		0.004 M		0.01 M		0.1 M		0.5 M	
Concentration	Time in hrs.	Osmose	Time in hrs.	Osmose	Time in hrs.	Osmose	Time in hrs.	Osmose	Time in hrs.	Osmose
$K_3Fe(CN)_6$	48	425	24	480	14	265	14	267	14	760
K_2SO_4	30	245	18	315	14	192	10	143	14	475
KCl	24	50	14	93	10	83	10	48	14	113.5
$CaCl_2$	10	13	8	3	12	−18	12	33	14	277
$AlCl_3$	16	14	18	77	14	93	18	356	20	1374
Sucrose	—	—	—	—	—	—	20	95	24	615

Osmose Results in the Rocking Cell

Readings were taken every half hour for the first two hours and then every two hours thereafter, until maximum osmose values were reached. The results at the end of the two hour period, twelve hour period and maximum osmose are given in Tables XI and XII. Comparisons of the effect of stirring and not stirring on the osmose of $AlCl_3$ and $K_3FeC_6N_6$ are shown in Figures 14 and 15, respectively.

The following generalizations concerning the effects of stirring on osmose were disclosed by the foregoing data.

1. The shape of the "initial osmose—concentration curves" (2 hour readings) and the "maximum osmose—concentration curves" for the potassium salts, were of the N type throughout and were more strongly accentuated than when the solutions were not stirred.

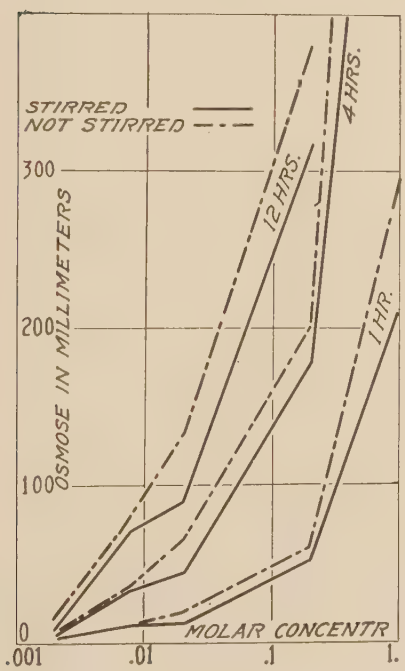

Fig. 14

Osmose Rate of $AlCl_3$ comparing Effect of Stirring vs. not Stirring Solutions

2. With dilute solutions stirring increased both the initial and maximum osmotic effects in the case of KCl, $CaCl_2$, and K_2SO_4, but decreased the effect with $AlCl_3$ and the maximum effect with $K_3FeC_6N_6$.

3. With concentrated solutions of electrolytes, greater than 0.1 M, stirring had but little influence on either the initial rate or maximum osmose.

4. Stirring produced a tendency toward the N shaped curve even in the case of $AlCl_3$ which tendency hitherto had not been observed.

5. With sucrose solu-

tions, stirring increased the initial osmose rate, but decreased the maximum osmose.

6. The above results are in harmony with the hypothesis that passage of solute through the membrane is largely responsible for the appearance of the N shaped curve in osmosis through collodion membranes.

Passage of Salt through the Membrane during Osmose in the Rocking Cell

For the purpose of measurement of the concentration of solute in each compartment during the osmotic process, the specific conductance of the respective solutions was determined. The specific conductance of the various electrolytes was calculated at all known dilutions from molar and equivalent conductivity data already published by Kohlrausch[69] and Jones.[70]

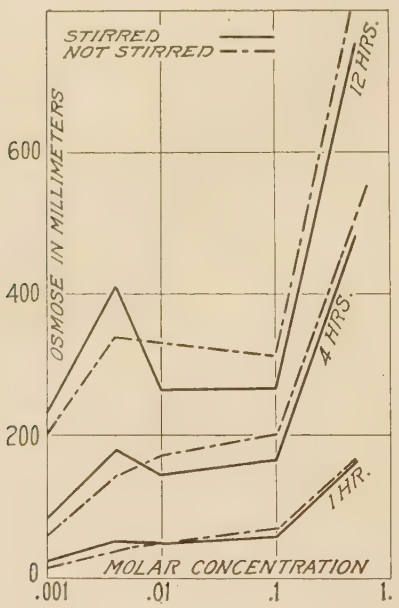

Fig. 15

Osmose Rate of $K_3Fe(CN)_6$ comparing Effect of Stirring vs. not Stirring Solutions

It was originally planned to determine the hydrogen ion concentration of each compartment as osmose developed. It was believed that this might throw some light on the problem. This would be of particular interest in cases of highly hydrolyzable salts, such as $AlCl_3$, where the HCl undoubtedly passes into the water compartment more rapidly than $Al(OH)_3$. These data could not be obtained in the time available for this research, but a correction can be applied to the conductivity

[69] Kohlrausch and Holborn: "Leitvermögen der Elektrolyte" (1898).

[70] Jones: Carnegie Institute of Washington, Publ. **170** (1912).

measurements hereinafter given, from data which may be presented at some future time.

The ratio of salt concentrations on the two sides of the membrane was calculated from conductivity measurements for the two hour period and also for the maximum osmose period. Several experiments continued beyond the maximum

TABLE XIII

Molar Concentrations of Solutions Two Hours after starting Osmose Experiment

Rocking Cell

Salt solution	Initial molar conc. of salt	Molar conc. of salt. Compartment C_1	Molar conc. of salt. Compartment C_2	Ratio C_1/C_2
$K_3FeC_6N_6$	0.001	0.000981	0.0000212	46.3
	0.004	0.003795	0.000218	17.4
	0.01	0.00919	0.000862	10.65
	0.1	0.0907	0.01036	8.76
	0.5	0.422	0.0597	7.29
K_2SO_4	0.001	0.000956	0.0000405	23.6
	0.004	0.003806	0.000248	15.3
	0.01	0.00907	0.000947	9.58
	0.1	0.0879	0.01201	7.31
	0.5	0.4151	0.0760	5.47
KCl	0.001	0.000977	0.0000768	12.7
	0.004	0.00347	0.000613	5.65
	0.01	0.00872	0.00152	5.75
	0.1	0.0784	0.0183	4.77
	0.5	0.423	0.1195	3.54
$CaCl_2$	0.001	0.000971	0.0000684	14.0
	0.004	0.00373	0.000443	8.42
	0.01	0.00899	0.00124	7.25
	0.1	0.0899	0.0124	7.25
	0.5	0.456	0.0661	6.89
$AlCl_3$	0.002	0.00178	0.000198	9.0
	0.008	0.00674	0.000671	10.03
	0.02	0.01601	0.00165	9.71
	0.2	0.1628	0.0219	7.43

osmose period showed that eventually identical concentration in both chambers was reached and at this point the osmose value had diminished to zero. The "least permeable" membranes were used throughout this part of the work.

Summary

The foregoing data warrant the following conclusions:

1. Stirring increased the rate of passage of all electrolytes through the membrane at all concentrations. The relative increase in diffusion rate due to stirring was greatest in dilute solutions.

TABLE XIV

Molar Concentrations of Solutions when Maximum was registered Rocking Cell

Salt solution	Initial molar conc. of salt	Molar conc. of salt. Compartment C_1	Molar conc. of salt. Compartment C_2	Ratio C_1/C_2
$K_3FeC_6N_6$	0.001	0.000761	0.000183	4.16
	0.004	0.002378	0.001384	1.72
	0.01	0.00595	0.003876	1.53
	0.1	0.0635	0.0438	1.45
	0.5	0.2973	0.2128	1.40
K_2SO_4	0.001	0.00746	0.000276	2.70
	0.004	0.002526	0.001662	1.52
	0.01	0.005895	0.00424	1.39
	0.1	0.0676	0.03868	1.75
	0.5	0.2966	0.2190	1.35
KCl	0.001	0.000640	0.000471	1.356
	0.004	0.002315	0.001755	1.320
	0.01	0.00612	0.00410	1.493
	0.1	0.0546	0.0426	1.281
	0.5	0.2765	0.2338	1.182
$CaCl_2$	0.001	0.000792	0.000237	3.34
	0.004	0.003024	0.001237	2.45
	0.01	0.00618	0.00420	1.47
	0.1	0.0656	0.0432	1.52
	0.5	0.3182	0.2300	1.38
$AlCl_3$	0.002	0.00121	0.000714	1.70
	0.008	0.00445	0.003017	1.47
	0.02	0.0088	0.00658	1.65
	0.2	0.1154	0.0803	1.44

2. The rate of passage of solutes into the water compartment was greater for concentrated solutions than dilute, but in no case proportional to concentration, except in two cases with $CaCl_2$.

3. In the region of 0.01 M concentration, the percent

increase in mols of salt passing through the membrane in two hours, due to stirring, was as follows: KCl 140, K_2SO_4 13, $K_3FeC_6N_6$ 63, $CaCl_2$ 72, $AlCl_3$ 95.

4. The ratio of concentrations of solute in the two compartments decreased in magnitude as osmose progressed. In

TABLE XV

Millimols of Salt passing through Least Permeable Membrane into Water Compartment during Two Hour Osmose Period

Salt	Initial molar conc. in salt compartment	Stationary cell A	Rocking cell B	$\frac{B}{A}$
$K_3FeC_6N_6$	0.001	———	0.00036	——
	0.004	0.0015	0.00371	2.46
	0.01	0.0090	0.01465	1.62
	0.1	0.164	0.1760	1.07
	0.5	———	0.9840	——
K_2SO_4	0.001	———	0.00069	——
	0.004	0.0034	0.00421	1.23
	0.01	0.0144	0.0163	1.13
	0.1	0.1803	0.2040	1.15
	0.5	———	1.291	——
KCl	0.001	———	0.00130	——
	0.004	0.0020	0.0104	5.20
	0.01	0.0107	0.0258	2.41
	0.1	0.217	0.3110	1.33
	0.5	———	2.032	——
$CaCl_2$	0.001	———	0.00118	——
	0.004	0.00275	0.00755	2.76
	0.01	0.01225	0.02105	1.73
	0.1	0.199	0.2105	1.05
	0.5	———	1.125	——
$AlCl_3$	0.002	———	0.00336	——
	0.008	0.00587	0.01141	1.94
	0.02	0.0234	0.02801	1.21
	0.2	0.282	0.3722	1.32

concentrated solutions this ratio approached 1:1 (approximately 1:1.4) at the maximum osmose period. For more dilute solutions, this ratio remained much greater.

5. With potassium salts, the relation of anion valence to rate of passage of electrolyte through the membrane showed

the following order in each case: $Cl' > SO_4'' > FeC_6N_6''$. This order was the same at all concentrations and was the inverse of the order of magnitude of maximum osmose. With chlorides, the cation order was $K > Ca > Al$ at all concentrations. This cation order was the inverse of the order of magnitude of maximum osmose in concentrated solutions. The above *orders* were the same as those obtained when the solutions were not stirred.

6. Stirring does accentuate the N shaped osmose curve.

VI. GENERAL SUMMARY.

1. The theory of anomalous osmose as advanced by Bartell and co-workers has been examined with respect to collodion membranes and found to apply.

2. Certain anomalous effects involving time as a factor in their appearance (the N shaped curves in the advance stage of osmose), not directly covered by the above theory, have been shown to be due to the passage of solute through the membrane into the water compartment. This materially alters the potential and concentration gradients across the membrane and gives the observed abnormal osmotic effects.